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Modeling of band offsets in GaN based heterostructures

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Abstract. We present a tight binding modeling of the band offsets of GaN based heterostructures. The model considers the nonorthogonality of the sp^3 set of orbitals of adjacent atoms and spin-orbit coupling and uses the Hartre–Fock atomic energies and interacting matrix element, obtained by fitting existing band structures for bulk materials, to determine the valence band energies at 0 K and 1 Bar, which are screened by the optical dielectric constants of bulk materials at any temperature, pressure, strain, and composition. The model compares very well with experiment for the valence and conduction band offsets of GaN based and many other heterostructures.

Introduction

The band offsets appearing at heterointerfaces dominate various device properties such as injection efficiency in heterojunction bipolar transistors (HBT) and the carrier confinement in modulation doped FETs (MODFETs) [1]. The need for precise and reliable prediction of band offsets has received the considerable attention of the solid state device scientists and engineers over the years (see Ref. [2] for a detailed discussion). In this article, the band offsets at GaN based heterointerfaces are determined using the extended tight binding model [3]. The presented model includes the overlapping of hybrids at neighboring bonds and anti-bonds such that it cannot simply be absorbed into a re-scaling of other parameters to find the valence band energies which are screened by the optical dielectric constants of constituents which are temperature, pressure, interface strain, and alloy composition dependent.

1. Extended tight binding modeling of band offsets

Consider the formation of bonding and antibonding states for a binary semiconductor from isolated c-cation and a-anion atoms. One uses the linear combination of bond orbitals sp^3 hybrids of the s- and p-states to write a bond orbital wave function as $|\phi_{\text{hac}}\rangle = u_c|\phi_{\text{ha}}\rangle + u_a|\phi_{\text{hc}}\rangle$ [3]. Here $|\phi_{\text{h}}\rangle = \frac{1}{2}(|s\rangle + \sqrt{3}|p\rangle)$ is the wavefunction of the sp^3 hybrid which has the expectation value of $\epsilon_{\text{h}} = \langle \phi_{\text{h}} | H | \phi_{\text{h}} \rangle = (\epsilon_s + 3\epsilon_p)/4$ and u_c and u_a are the coefficients. $\epsilon_s = \langle \phi_s | H | \phi_s \rangle$ and $\epsilon_p = \langle \phi_p | H | \phi_p \rangle = \epsilon_{\text{op}} + \Delta/3$ are Hartree-Fock free atomic term values, where $\Delta/3$ is the crystal field splitting energy of p-states [4] and ϵ_{op} is the value of ϵ_p without the splitting. By using the variational principle the bond and antibond orbital energies can be obtained and minimizing the expectation value E with respect to coefficients u_c and u_a ($\partial E / \partial u_c = 0$ and $\partial E / \partial u_a = 0$) one obtains a set of two linear equations for u_c and u_a . The solutions of this set of equations are the energies of antibonding and bonding hybrids, obtained from: $\sum_{i,j=1}^2 (H_{ij} - ES_{ij}) = 0$. Here $H_{11} = \epsilon_{\text{hc}}$ and $H_{22} = \epsilon_{\text{ha}}$ are the hybrid energies, $H_{12} = H_{21}^* = V_{\text{sp}^3}$ is the interaction matrix and $S_{12} = S_{21}^* = S_{\text{sp}^3}$ and $S_{11} = S_{22} = 1$ are the overlap integrals between orbitals on adjacent anion and cation and on the same cation or anion. The interaction between the hybrids on

the same anion and cation, or between the bond and neighboring antibonds will broaden the hybrid energies into valence and conduction bands at $k=0$, and for the valence band energy is written as [3]:

$$E_v(\Gamma_{8v}) = E_b - E_{mv} = \frac{\epsilon_{hc} + \epsilon_{ha}}{2(1 - S_{sp^3}^2)} - \frac{V_{sp^3} S_{sp^3}}{(1 - S_{sp^3}^2)} - \Delta E_h - E_{mv} \quad (1)$$

$$\Delta E_h = \frac{1}{2(1 - S_{sp^3}^2)} \left[(\epsilon_{hc} - \epsilon_{ha})^2 - 4(\epsilon_{ha} + \epsilon_{ha}) S_{sp^3} V_{sp^3} + 4\epsilon_{hc}\epsilon_{ha} S_{sp^3}^2 + 4V_{sp^3}^2 \right]^{1/2} \quad (2)$$

where ΔE_h is the hybrid bonding gap. Minimizing ΔE_h relative to lattice constant a ($(\partial \Delta E_h)/(\partial V_{sp^3}) = 0$) one obtains the overlap integral: $S_{sp^3} = 2V_{sp^3}(\epsilon_{hA} + \epsilon_{hB})$, where $V_{sp^3} = k/a^2$, with coefficient $k \approx 107$ obtained from the fitting to band structure of bulk semiconductors. The metallization contribution to the broadening of bonding energy E_b into valence band energy E_v is [4]: $E_{mv} = (1/2)[(1 + \alpha_p)V_{1c} + (1 - \alpha_p)V_{1a}] + 2\alpha_c V_1^x$, where $V_1 = (\epsilon_p - \epsilon_s)/4$ characterizes the s-p splitting in the free atom. $V_1^x = -\frac{1}{4}(V_{ss} + 2V_{sp}/\sqrt{3} - V_{pp})$ is the additional contribution to the matrix elements between nearest neighbor bonds. Since the u_c/u_c ratio defines ionic character of hybrid, the polarity α_p and covalency α_c of hybrid bond are defined as [3]: $\alpha_p = u_c/(u_c^2 + u_a^2)^{1/2}$ and $\alpha_c = (1 - \alpha_p^2)^{1/2}$. Demanding that $|\phi_{hac} \rangle$ is normalized, $\langle \phi_{hac} | \phi_{hca} \rangle = u_c^2 + u_a^2 + 2u_c u_a S_{sp^3} = 1$, coefficients u_c and u_a can be obtained by solving the secular equations using the bonding energy $E = E_b$ giving u_c and u_a for the bonding hybrid:

$$u_c = \frac{(V_{sp^3} - S_{sp^3} E)}{U_{sp^3}}, \quad u_a = \frac{(E - \epsilon_{hc})}{U_{sp^3}} \quad (3)$$

$$U_{sp^3} = \left[(V_{sp^3} - S_{sp^3} E)^2 + (\epsilon_{hc} - E)^2 - 2S_{sp^3} (E - \epsilon_{hc}) (V_{sp^3} - S_{sp^3} E) \right]^{1/2} \quad (4)$$

The band offset at A/B heterointerface is then found from the following equation

$$\Delta E_v = \left(\frac{E_v}{\epsilon_\infty} \right)_B - \left(\frac{E_v}{\epsilon_\infty} \right)_A \quad (5)$$

where ϵ_∞ the optical dielectric constant of the constituent semiconductors. The conduction band offsets at high symmetry points Γ_{6c} , L_{6c} , and X_{6c} can be obtained from $\Delta E_{ci} = \Delta E_{gi} - \Delta E_v$, where ΔE_{gi} ((with $i = \Gamma, L, X$)) is the bandgap difference. The conduction and valence band energies, defined as the standard state chemical potentials, at any temperature and pressure can be written as [5]:

$$E_c(T, P) = E_c(0, P_0) + C_{cp}^0 T(1 - \ln T) - \frac{a_c}{B} \left[P - \frac{P^2}{2B} - \frac{(1 + B')P^3}{6B^2} \right] \quad (6)$$

$$E_v(T, P) = E_v(0, P_0) + C_{vp}^0 T(1 - \ln T) + \frac{a_v}{B} \left[P - \frac{P^2}{2B} - \frac{(1 + B')P^3}{6B^2} \right] \quad (7)$$

where $P_0 = 1$ Bar and P is the applied pressure. $a_c = -B(\partial E_c / \partial P)$ and $a_v = B(\partial E_v / \partial P)$ are deformation potentials of E_c and E_v , with bulk modulus B and its derivative $B' = \partial B / \partial P$. $C_{cp}^0 = C_{np}^0 - C_{op}^0 = -C_{pp}^0 + \Delta C_p^0$ and $C_{vp}^0 = C_{pp}^0$ standard heat capacities of conduction electrons and valence holes, where $C_{ip}^0 = C_{np}^0 = C_{pp}^0 = (5/2)k_B$ and

$C_{0P}^0 = C_{nP}^0 + C_{pP}^0 - \Delta C_P^0$, with ΔC_P^0 being the heat capacity of reaction which is obtained from fitting of the bandgap $E_{gi}(T, P) = E_{ci}(T, P) - E_v(T, P)$ to its corresponding measured value [6]. The effects of interface strain on ΔE_c and ΔE_v can be found by substituting $P = -2B_f C_f \epsilon_{f\perp}$ for heterolayer and $P = -3B_s \epsilon_s = 0$ for substrate for a (001) growth, written as [3]:

$$\Delta E_v(T, \epsilon) = \Delta E_v(T) - 2a_{vf} C_f \epsilon_{f\perp} [1 + C_f \epsilon_{f\perp}] - 2a_{vf} C_f \epsilon_{f\perp} \frac{2(1 + B'_f)}{3} C_f^2 \epsilon_{f\perp}^2 \quad (8)$$

$$\Delta E_{ci}(T, \epsilon) = \Delta E_{ci}(T) + 2a_{cf} C_f \epsilon_{f\perp} [1 + C_f \epsilon_{f\perp}] - 2a_{cf} C_f \epsilon_{f\perp} \frac{2(1 + B'_f)}{3} C_f^2 \epsilon_{f\perp}^2 \quad (9)$$

where $\epsilon_{f\perp} = (a_{f\perp} - a_f)/a_f$. Here $a_{f\parallel} = a_s$ and $a_{f\perp} = a_f[1 - D_f(a_{f\parallel} - a_f)/a_f]$ and $D_f = 2C_{12}/C_{11}$ with C_{11} and C_{12} the elastic constants.

The valence band offset at $A_x B_{1-x} C/BC$ heterointerface is obtained by taking anion energy as $\epsilon_{pa}(C)$ and cation energy as $\epsilon_{pc}(x) = x\epsilon_{pc}(A) + (1-x)\epsilon_{pc}(B)$ and lattice constant $a(x) = xa(AC) + (1-x)a(BC)$, in calculating $E_v(x)$ of $A_x B_{1-x} C$ ternary. The composition effects on conduction band offset $\Delta E_c(x)$ can be obtained with the use of Vegard's rule and Kane's $\mathbf{k} \cdot \mathbf{p}$ model for semiconductors [1, 7]: $(1/m_n(x)) = 1 + (P^2(x)/3)[(2/E_g(x)) + 1/(E_g(x) + \Delta(x))]$, where $m_n(x) = m_{nA} m_{nB} / (x m_{nB} + (1-x)m_{nA})$ is the ternary electron effective mass obtained from Vegard's rule [1, 7]. m_{nA} and m_{nB} are the electron effective masses of binaries A and B. $P(x) = xP_A + (1-x)P_B$ is the momentum matrix and $\Delta(x) = x\Delta_A + (1-x)\Delta_B$ is the spin-orbit energy. P_A and P_B of binaries A and B are obtained from Kane's equation with measured $m_n(x)$ and $\Delta(x)$ for $x=0$ and 1 [6]. Kane's equation can be rewritten in a quadratic form for bandgap $E_{g\Gamma}$, whose positive root gives [3]:

$$E_{g\Gamma}(x) = \frac{3/y(x) - \Delta(x)}{2} + \frac{1}{2} \left[(\Delta(x) - 3/y(x))^2 + 8\Delta(x)/y(x) \right]^{1/2} \quad (10)$$

where $y(x) = 3(1 - m_n(x))/m_n(x)P^2(x)$. A similar expression can be found for E_{gL} bandgap using equation (31) of Adachi [7]. The indirect gap E_{gX} is determined from $E_{gX}(x) = E_{g\Gamma}(x) + (E_{gXA} - E_{g\Gamma A})x + (E_{gXB} - E_{g\Gamma B})(1-x)$. Here E_{gXA} , E_{gXB} , $E_{g\Gamma A}$, and $E_{g\Gamma B}$ are the indirect and direct bandgaps of binaries A and B.

Results and discussion

The valence band offsets at AlN/GaN, GaN/InN and AlN/InN and GaN/GaP heterointerfaces are obtained from Eq. (5) using the Hartree-Fock free term values [4], measured bandgaps, and the spin orbit splitting energies [4, 6]. Predictions of this work (ETB1) are given in Table I, compared with those of p-p extended tight binding model (ETB1) [8], self consistent tight binding model (SCTB) [9], linear muffin thin orbital model (LMTO) [10], and the first principles electronic structure model (FPES) [11] against the experiment [12, 13]. The model predictions are compatible with those of quantum mechanical models, which are based on the elaborate band structure calculations of heterojunction components.

The model was also applied to III-Nitride based ternary/binary heterostructures to determine the composition effects on band gaps and band offsets. The parameters used for Al-GaN/GaN heterostructure are: $m_n/m_0=0.15$ and 0.25 , $m_p/m_0=0.40$ and 0.70 , $\Delta_s/\text{meV}=11$ and 19 , and $E_{g\Gamma}/\text{eV}=6.20$ and 3.39 for GaN and AlN, respectively [14, 15]. Although there is no data available for ΔE_v at $Al_x Ga_{1-x} N/\text{GaN}$ heterointerface, prediction of Eq. (10) for the direct bandgap $E_{g\Gamma}$ of $Al_x Ga_{1-x} N$, is found to be in good agreement with experiment[14].

Table 1. Comparison of this work (ETB1) with those of p-p extended tight binding (ETB2) model [8], self consistent tight binding model (SCTB) [9], linear muffin thin orbital model (LMTO) [10], and first principles electronic structure model (FPES) [11], against the measured valence band offsets [12, 13]. (All values are in eV.)

System	ETB1	ETB2	SCTB	FPES	LMTO	Experiment
AlN/GaN	0.26	0.33	0.17	0.84	0.85	0.57 ± 0.22 [12]
AlN/InN	1.52	1.66	0.13	1.04	1.09	1.81 ± 0.20 [12]
GaN/InN	1.27	1.33	-0.04	0.26	0.51	1.05 ± 0.25 [12]
GaN/GaP	1.84	1.74	1.89	1.72	—	2.30 ± 0.6 [13]

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